REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*
03-10-2010

2. REPORT TYPE
Final Report

3. DATES COVERED *(From - To)*
7/1/2008 – 6/30/2009

4. TITLE AND SUBTITLE
" Vibrational Spectroscopic Analysis on the Deformational Behavior of Hybrid Polymers”

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-08-1-0347

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Andre Lee

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Michigan State University
AND ADDRESS(ES)
Department of Chemical Engineering and
Materials Science
Rm. 2527 Engineering Bldg.
East Lansing, MI. 8824
(517)355-5112

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AF Office of Scientific Research
875 N. Randolph St., Suite 325, Rm 3112
Arlington, VA. 22203
Dr. Charles Y-C. Lee
(703)696-7779

10. SPONSOR/MONITOR’S ACRONYM(S)
AFOSR/NL

11. SPONSOR/MONITOR’S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release distribution is unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
Under this equipment grant, we are to acquire a unique characterization facility needed fordetermining sub-molecular level changes in the atomic bonding responsible for the enhanced performance of materials reinforced with a new class of nano-structured, hybrid chemicals; polyhedral oligomeric silsesquioxanes (POSS). This facility is vital to the PI’s current AFOSR and AFRL-PRSM projects because it will expand the use of POSS in both high temperature polymeric matrix composites and engineering elastomers. This effort is needed for a fundamental advancement of our understanding for the synergistic performance enhancement in the use of nano-structured hybrid chemicals with organic materials. Under this effort, we had purchased 1) an upgrade the existing Fourier transform infrared spectrometer (FT-IR) equipped with a new detector, 2) a micro-Raman spectrometer with 3 different excitation lasers covering from UV to near-IR range, and 3) a custom heated deformation stage. This unique facility with these state-of-the-art spectroscopic techniques will enable a direct measurement on the shifts of vibrational frequencies which are associated with specific molecular segments as the material experiences an externally imposed field, e.g., thermal or mechanical loads. The spectroscopic technique is also a non-destructive method. This information is invaluable as we seek to understand the molecular origins behind the observed performance enhancements in a variety of materials which have been reinforced by functionalized, nano-structured hybrid chemicals such as POSS.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
					Andre Lee
a. REPORT	b. ABSTRACT	c. THIS PAGE		6	19b. TELEPHONE NUMBER *(include area code)* 517-355-5112

Air Force Office of Scientific Research

Final Report

Vibrational Spectroscopic Analysis on Deformational Behavior of Hybrid Polymers

10 March 2010

Andre Lee
Department of Chemical Engineering and Materials Science
Michigan State University
Rm 2527 Engineering Bldg.
East Lansing, MI. 48824
leea@egr.msu.edu

Submitted to
Dr. Charles Y-C Lee
AFOSR/NL
875 N. Randolph St.
Suite 325, Rm 3112
Arlington, VA. 22203
Charles.lee@afosr.af.mil

Vibrational Spectroscopic Analysis on Deformational Behavior of Hybrid Polymers

Andre Lee, Michigan State University

Overall Objective

The objective of this grant is to expand the molecular vibrational spectroscopy facility at Michigan State University that enables the investigation on the deformation behavior of polymers containing hybrid inorganic-organic, nano-structured chemicals. In addition, mapping capability of micro-Raman spectroscopy will enable the study on properties changes at specific locations. This knowledge is needed to better understand the degradation mechanisms in assessing the service durability of fiber-reinforced composites as relating to Air Force applications.

Status of Final Report

This equipment grant aims to improve and expand the molecular vibration facility at Michigan State University to explore the use of hybrid inorganic-organic, nano-structured chemicals in various polymers. More specifically, we will explore the use of nano-structured chemicals such as Polyhedral Oligomeric Silsesquioxane (POSS) in polymers. This nano-structured chemical "reinforcement" approach not only retains the light-weight nature of organic polymers, but also substantially improves many other desirable performance qualities, i.e., high temperature mechanical properties and oxidative stability, surface durability, etc., in comparison to conventional organic polymers. The three-dimensional nature and nanoscopic size of POSS are the key contributors to the material property improvements observed through POSS incorporation. Under this equipment grant, we had acquire (1) new IR detector which was installed in the existing FT-IR spectrometer with microscope attachment (100 microns resolution); (2) New micro-Raman with 3 laser lines (320 nm, 540nm and 1069 nm). The micro-Raman has better than 5 microns resolution; (3) heated-deformation stage with temperature capability up to 500^{o}C.

Background

The field of inorganic-organic hybrid materials has grown dramatically over the last several years. This interest stems from the desire to increase the material performance by combining the ease of processibility of organic polymeric materials with the excellent high temperature performance of inorganic materials. To apply this inorganic-organic hybrid approach to a wide variety of organic polymer systems, it is necessary to build and control the molecular structure at several length scales, thereby tailoring the hybrid materials to the targeted organic polymers using systematic chemical and material principles. Nano-structured hybrid chemicals represent such an approach. Nano-structured hybrid chemicals are defined by the following features. (1) They are single molecules consisting of both inorganic and organic components and not compositionally fluxional assemblies of both. (2) They possess polyhederal geometries with well-defined three-dimensional shapes. Clusters are good examples of polyhedral geometries where planner hydrocarbons, dendrimers and particulates are not. (3) They have a nanoscopic size that ranges to a few nanometers. Hence, they are larger than small molecules, but smaller than the coil dimensions of many high molecular weight polymers. (4) They have systematic chemistries that enable control over stereo-chemistry, reactivity and physical properties. Nano-structured hybrid chemicals represent a merger between traditional organic chemicals and inorganic materials which result in compositions that are truly hybrid (organic-inorganic). Currently, one of the best developed nano-structured chemicals (from the point-of-view of chemical varieties and cost prospective) is based on polyhedral oligomeric silsesquioxanes (POSS).

In our research effort to better understand the use of POSS, we had incorporated them in high temperature thermosetting oligoimides as well as engineering thermoplastic elastomers.

High temperature polyimide matrix composites

One approach investigated in our effort to enhance thermal and mechanical performance of thermosetting materials is to increase the overall crosslink density. The POSS framework provides multiple reaction sites associated with a common Si-O core. Furthermore, due to the di-functional nature of the oligoimide used and the nanoscopic size of the Si-O core, the increase in overall crosslink density of this hybrid polymeric network has a minimal effect on the molecular weight and its distribution between crosslink junctions. The vibrational spectroscopy is used to study many different aspects from curing mechanisms to degradation mechanisms due to exposure to the service environments.

Engineering Thermoplastic Elastomers

Block copolymers have been widely used as engineering thermoplastic elastomers since the early 1970s, and more recently they are being considered for applications in nanotechnology. The main focus of their nanotechnology application is rooted in their ability to form a self-assembled microstructure on the nanometer scale, which has lead to applications in membranes, templates for nanoparticle synthesis, photonic crystals, high-density information storage media and beyond. The nanostructured, functional chemicals can be grafted on to specific phase of a block copolymer. In this effort, the PI investigated the surface chemistry of the grafted nanostructures on the host block copolymer morphology. More specifically, the interaction between the chemical substituents of POSS, i.e., phenyl (Ph) and isobutyl (iBu), to the ungrafted portion of the host polystyrene endblocks, the morphology and mechanical behavior of POSS-grafted SBS can be significantly altered. This knowledge is expected to have a significant benefit in the use of SBS as engineering elastomers.

Details on the Equipment Acquired

Nano-structured chemicals such as POSS offer systematic chemistries that enable control over stereochemistry, reactivity and physical properties. The hybrid (inorganic-organic) composition of POSS enables it to occupy a very unique and dramatically enhanced property space relative to traditional hydrocarbons and inorganic materials. An important benefit is that it yields material formulations with excellent thermal and oxidative stability, which is largely attributed to the inorganic component. However, the architecture of the POSS molecule also plays a significant role in the overall TOS of hybrid polymeric networks. The organic portion of POSS provides various chemical pathways for incorporating and reacting with traditional organic components and organic polymers. These pathways are expected to be influenced by the reactivity between the organic portion attached to the SiO core of the POSS and the host organic oligomers. Hence, it is suggested that the final network morphology is influenced by the molecular architecture of the POSS used. Vibrational spectroscopy such as infrared and Raman offers the most direct route to monitor the network formation process and to provide a measure of internal strain/stress as these hybrid systems undergo chemical reactions to form networks. The level and the rate of change of this internal strain/stress are known to affect the performance of the cured network.

Another important factor in preserving composite performance is the integrity of the interface between the carbon fiber and the matrix. The use of laser in Raman spectroscopy and infrared microscopy will enable us to focus at this specific interface region. From the results obtained from the vibrational spectroscopic analysis, we expect to monitor the degradation kinetics as well as the strain at the molecular-level at this highly specific region. This molecular-level information is critical in order to understand the micromechanics of fiber reinforced composites. The spectroscopic results in combination with results obtained using solid-state dynamic mechanical analysis, we will develop molecular-level micromechanics models that are capable of describing the stress-strain constitutive relationship as the fiber reinforced POSS-oligoimide matrix composite undergoes thermal, mechanical and oxidative aging.

In the study of block copolymer grafted with POSS, the POSS is covalently bonded to a specific block. In effect, we were able to control the entropic contribution and the energetic interactions between different organic blocks by changing the chemical substituent of POSS used. This approach offers a systematic change in the morphology of block copolymers, thereby achieving a desired performance at different regimes of interest. The unique feature of vibrational spectroscopic analysis is the ability to examine the effect of external stimuli on different segments of the same molecule. Therefore, we will able to utilize this unique feature to examine deformation responses attributed to different blocks. This knowledge is of significant benefit to increase performance space of engineering elastomers through nanotechnology, which is of current interest of AFRL-PRSM.

Three major components were acquired under this equipment grant. (1) new IR detector which was installed in the existing FT-IR spectrometer with microscope attachment (100 microns resolution); (2) New micro-Raman with 3 laser lines (320 nm, 540nm and 1069 nm). The micro-Raman has better than 5 microns resolution; and (3) heated-deformation stage with temperature capability up to 500^{o}C.

The new IR detector offers a continuous measurement of samples under either curing or durability testing. This is a significant improvement over our old liquid N_2 detector. Raman spectroscopy in combination with IR provides a complete picture on the molecular vibrational information. The micro-Raman with multiple excitation lasers ranging from UV to near-IR enables the collected Raman signals to be free of fluorescence. This broad range of excitation wavelengths is necessary as we expect to apply this technique to broad spectrum of materials from metals, ceramics, electronic materials, biomaterials, polymers, etc.

A heated deformation stage enables us to study effect of external mechanical stimuli at different temperatures and air environments. Currently we are integrating the deformation mechanisms with the spectroscopic collection sequence. The extent of integration depends on the need of different materials and interests.